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On the Sensitivity in Fluorometry of Europium as Naphthoyltrifluoroacetate (Commemoration Issue Dedicated to Professor Tsunenobu Shigematsu on the Occasion of his Retirement)

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Note

**On the Sensitivity in Fluorometry of Europium
as Naphthoyltrifluoroacetate**

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The effect of various factors on the fluorescence intensity of europium naphthoyltrifluoroacetate was examined. Under the most sensitive condition of the instrument, a linear relationship between 0.02 and 0.1 ppb of europium was obtained. The S/N ratio of the fluorescence spectra was markedly improved by using a data processor.

KEY WORDS : Fluorometry/ Europium/ Adduct formation/

INTRODUCTION

Several β -diketonates of rare earths are known to fluoresce,^{1,4)} and this characteristic has been used for the very sensitive method of their determination. In our previous papers, spectrofluorometric determination of europium β -diketonates such as benzoyltrifluoroacetate⁶⁾ and naphthoyltrifluoroacetate⁷⁾ was investigated, where trioctylphosphine oxide was used to enhance the extraction of the chelate. In general, the sharp line emission observed when these β -diketonates were excited by u. v. light was dependent on the adduct formation of the chelates^{3,5)}; the adduct formation resulted in an enhanced fluorescence quantum yield. The present work dealt with the influences of the adduct formation, organic solvent, several other variables for the fluorometric determination, light sources such as xenon and mercury lamps, and data processing on the fluorescence intensity.

EXPERIMENTAL

Reagents.

2-Naphthoyltrifluoroacetone (NTFA) was synthesized by Claisen condensation from 2-acetonaphthone and trifluoroacetic acid.⁸⁾ The product was purified by recrystallizing more than twice from ethanol-water mixture.

A stock solution of europium was prepared by weighing out 99.9% europium oxide

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(dried in a vacuum desiccator, Shin-Etsu Chem. Ind. Co., Ltd.), dissolving with hydrochloric acid, evaporating to near dryness, and diluting with redistilled water.

Extraction solvents such as cyclohexane, benzene and chloroform were used after distillation. Tri-*n*-octylphosphine oxide (TOPO), Triphenylarsine oxide (TPAsO) and *o*-phenanthroline (*o*-phen) were used as an adduct-formation reagent.

The other chemicals were chemically pure or reagent grade materials.

Apparatus.

The fluorescence measurements were made with a Jasco fluorescence spectrophotometer, Model FP-550 (150 W xenon lamp) and Union Giken fluorescence recording spectrophotometer Model FS-401-01 (150 W xenon lamp) with a photon counting tube and data processor system, Model 77-02. The fused silica cell of 10 mm was used. For the pH measurement a Hitachi-Horiba pH meter, Model F-7ss was used.

General procedure.

All extractions were carried out in a 30ml centrifuge tube with the aid of a mechanical shaking device at room temperature. Equal volumes (usually 10 ml) of aqueous and organic phases were equilibrated for 30 min. The aqueous phase contained an appropriate amount of europium and acetic acid-sodium acetate buffer (0.05 M) as the buffer solution. The organic phase contained appropriate concentrations of NTFA and TOPO. After the solutions were centrifuged, the pH of the aqueous phase was measured. The organic phase was transferred to a 1 cm silica cell, and measured the fluorescence at 615 nm, using the rhodamine B solution as a standard.

RESULTS AND DISCUSSION

Of europium β -diketonates, 2-naphthoyltrifluoroacetone chelate displayed the very strong fluorescence, as shown in our previous papers,^{6,7)} the fluorometric method with NTFA was about 20-fold more sensitive than that with benzoyltrifluoroacetone. There-

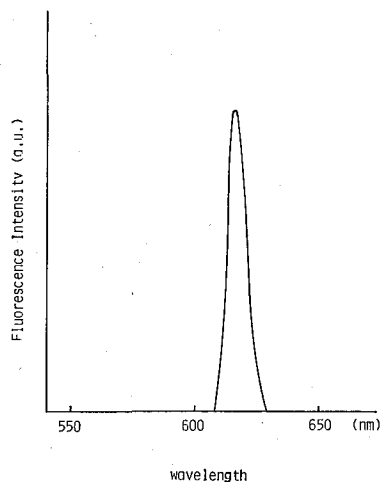


Fig. 1. Fluorescence spectrum of NTFA-europium-TOPO chelate.

Eu; 5 ppb, NTFA; 5×10^{-5} M, TOPO; 1×10^{-2} M, solvent; cyclohexane.

fore, NTFA was used throughout this experiment. The fluorescence spectra in NTFA-europium-TOPO system are shown in Fig. 1.

Chloroform, benzene, and cyclohexane were used to examine the effect of the extracting solvent on the fluorescence intensity of the europium chelate. Cyclohexane was convenient as the extracting solvent for the europium NTFA chelate, because the fluorescence intensity in cyclohexane was 30% higher and kept constant over a wider pH range than that in benzene. When chloroform was utilized for the organic solvent, europium ions were scarcely extracted between pH 4 and 6. In consideration of extractable pH range and sensitivity, cyclohexane was used throughout the other experiments.

Europium ions can be extracted in wider pH region with β -diketones by adding oxygen- or nitrogen-containing Lewis bases to the extraction system. This synergistic effect in solvent extraction is caused by the adduct formation between the europium β -diketonates and the Lewis base. Therefore, authors examined the effect of Lewis bases on the extraction pH range and fluorescence intensity of the europium chelate. TOPO, TPAsO and *o*-phen were chosen as the Lewis base, because a larger synergistic effect was expected by using such strong bases. Extraction curves of europium were

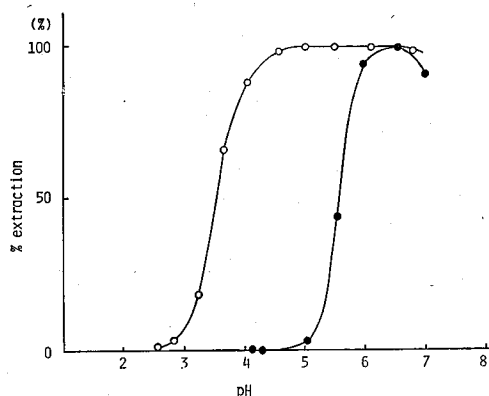


Fig. 2. Extraction curves of europium.
NTFA; 1×10^{-4} M,
○; 1×10^{-2} M TOPO in cyclohexane,
●; 1×10^{-3} M TPAsO in benzene.

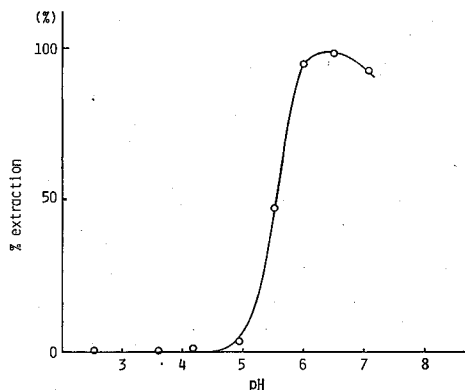


Fig. 3. Extraction curve of europium.
NTFA; 1×10^{-4} M,
○-phen; 1×10^{-3} M in benzene.

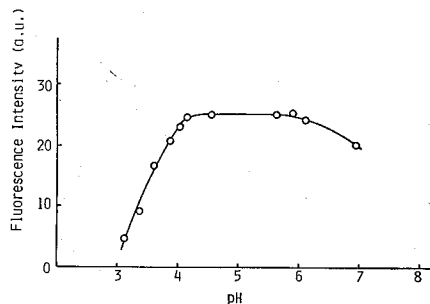


Fig. 4. Dependence of the fluorescence intensity of $\text{Eu}(\text{NTFA})_3 \cdot \text{TOPO}$ on the pH value.
Eu; 5ppb, NTFA; 1×10^{-4} M, TOPO; 1×10^{-2} M, solvent; cyclohexane.

shown in Figs. 2 and 3. TPAsO and *o*-phen were sparingly soluble in cyclohexane and readily soluble in benzene. Hence benzene was adopted in the extraction system using TPAsO and *o*-phen as the Lewis base. As shown in the figures, europium is quantitatively extracted above pH 4.5 for TOPO, while in the narrow pH range around pH 6.5 for TPAsO and *o*-phen. As the fluorescence intensity of the europium chelates was not very influenced by these three bases, TOPO was used in the following experiment. The dependence of the fluorescence intensity on the pH value was shown in Fig. 4 which displayed almost the same tendency to the extraction recovery of europium.

The effect of excess TOPO was studied by keeping the europium and NTFA concentrations constant at 3.3×10^{-8} and 10^{-4} M, respectively, and by varying the TOPO concentration. A nearly constant fluorescence intensity of europium was obtained in the concentration range of TOPO between 5×10^{-4} and 10^{-2} M. However, the fluorescence intensity increased markedly as the TOPO concentration increased over 10^{-2} M as shown in Fig. 5. This may be caused by the fact that the maximum number of TOPO bonding to one molecule of the europium β -diketonate is 2⁹⁾; 1:1 adduct of TOPO was mainly formed in a lower TOPO concentration and 1:2 adduct increased as the TOPO concentration increased.

The influences of the other variables such as NTFA concentration, temperature, irradiation time and foreign ions were the same to those described in the previous paper.⁷⁾ A plot of fluorescence intensity *vs.* europium concentration showed a linear relationship between 0.02 and 0.1 ppb. The calibration curve in Fig. 6 was made by using high sensitive cell holder and by measuring the intensity under the most sensitive condition of Jasco fluorescence spectrophotometer, Model FP-550.

Union Giken fluorescence recording spectrometer, Model FS-401-01 with a photo counting tube is provided with data processor system, Model 77-02. Figure 7 indicates the relationship between the gate time (1 gate time corresponds to 35 msec.) and the fluorescence spectra of europium chelate; the ratio of signal to noise of the fluorescence spectra was remarkably improved as the gate time increased from 1 to 20. The S/N ratio was also influenced by the scan number of data accumulation as shown in Fig. 8;

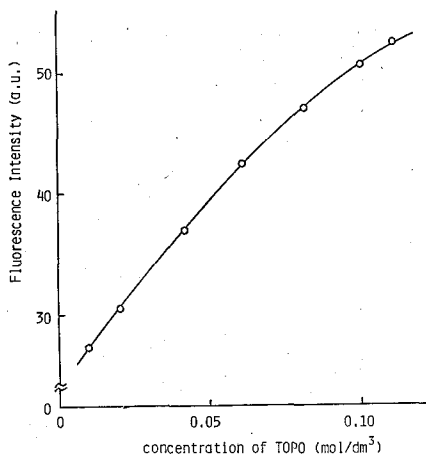


Fig. 5. Effect of TOPO.
Eu; 5 ppb, NTFA; 1×10^{-4} M,
solvent; cyclohexane.

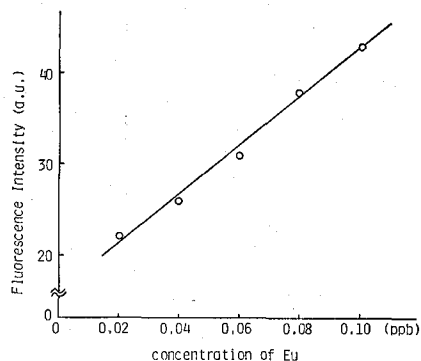


Fig. 6. Calibration curve of europium.
NTFA; 5×10^{-5} M, TOPO; 4×10^{-4} M,
solvent; cyclohexane.

On the Sensitivity in Fluorometry

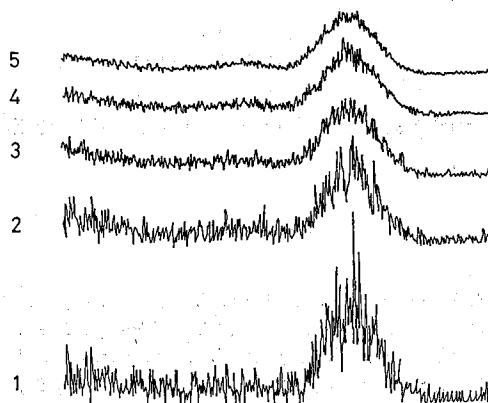


Fig. 7. The relationship between the gate time and the fluorescence spectra of europium chelate.

Eu; 5 ppb, NTFA; 5×10^{-5} M, TOPO; 2×10^{-2} M, scan number; 1.

Curve 1;	gate time 1,	sens.of recorder 0.1(V),
2;	" 2,	" 0.2(V),
3;	" 5,	" 0.5(V),
4;	" 10,	" 1.0(V),
5;	" 20,	" 2.0(V).

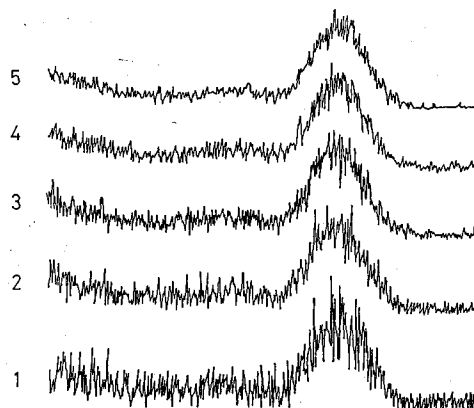


Fig. 8. The relationship between the S/N ratio and accumulation number.

Curve 1;	accumulation number 1,
2;	" 2,
3;	" 3,
4;	" 4,
5;	" 10.

Gate time; 1, others are the same as in Fig. 7.

as the number of accumulation grew, the S/N ratio underwent considerably improvement.

The considerable increment of fluorescence intensity was observed when a mercury lamp was used as a light source instead of the xenon lamp. However, the fluorescence

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lacked in stability probably on account of the unsuited mounting of the light source.

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